Branching Ratios of the Circular Dichroism at Rare Earth L_{23} Edges

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The branching ratios in the circular dichroism of the rare-earth L_{23} edges are explained in a model where the $5d$ band is empty in the ground state. In the final state the $5d$ radial wave function contracts not only by the $5d$-$4f$ spin-spin interaction but by the complete exchange interaction. This explains the L_3/L_2 ratios, the relative magnitude of the quadrupole contribution, and the dispersive shape of the signal in ionic compounds. [S0031-9007(97)02353-3]

Since the first observation of x-ray magnetic circular dichroism (XMCD) in the L_{23} edges [1] of rare-earth compounds extensive series of experiments have been performed [2–4]. The transition of a $2p$ electron into the $5d$ shell seemed to make these spectra promising for the study of the role of the $5d$ electrons in the complex magnetic phenomena of the rare-earth compounds. The interpretation of the spectra has always been a source of debate because they did not follow simple rules. In the description of x-ray absorption from the $2p$ shell into the valence band, one has to distinguish two contributions.

First, it was found that just below the edge jump there is a structure in the dichroism due to quadrupole transitions $2p \rightarrow 4f$ [5]. The quadrupole nature was confirmed by resonant Raman spectroscopy [6] and the observation at low temperatures of an angle dependence different from the only possible dipole dependence [7], i.e., $\cos\theta$. A disturbing point that remained was that a quadrupole component was never clearly observed in the L_2 edge.

Second, the dominant contribution in the isotropic spectrum comes from dipolar transitions into the nearly empty $5d$ shell. In a one-particle framework, XMCD results from a difference in occupation of spin-up and spin-down $5d$ bands [5,8]. By inclusion of not only the spin-spin interactions but also the strong orbital polarization due to the exchange interaction with the $4f$ shell, in addition to the contribution by $5d$ spin-orbit interaction, Jo and Imada [9] also produced a reasonable description of the variation of the size of the L_3/L_2 ratio. However, experimentally, the sign of the integrated intensity of the XMCD appeared to be opposite to that expected from this model. This implies that the polarization of the $5d$ electrons in the ground state does not explain the circular dichroism signal. The sign change could be explained [8] by the observation that the orbitals with the spin parallel to the $4f$ spin are contracted relative to orbitals with the opposite spin, due to the attraction of this band by the spin of the $4f$ shell. This contraction gives rise to a larger $2p \rightarrow 5d$ dipole transition matrix element. As a consequence, the band with spin parallel to the $4f$, although it should contain fewer holes, gives a larger absorption. This theory is confirmed by the fact that in f^0 and f^{14} compounds this sign reversal is not present.

For the branching ratio of the dichroism signals in the L_3 and L_2 edges, band structure always gives a value of -1, with a small deviation due to the presence of $5d$ orbital moment in the ground state. This should be compared with experiment [2–4] where in early rare earths, L_2 is up to 8–10 times larger than the L_3, whereas in the late part of the series L_3 is larger by a factor of up to 10–15. This effect was also observed in σ to π scattering at the $2p$ resonance of rare-earth compounds. The cross section for this scattering is about the absolute square of the circular dichroism in absorption and, indeed, L_3/L_2 ratios of ~0.01 to 50 have been observed [10].

Recent data on insulating compounds show dispersive line shapes, i.e., with approximately equal positive and negative parts, that can be described accurately by atomic calculations assuming a $5d^0$ ground state [11]. Although, according to the x-ray absorption spectroscopy (XAS) sum rules [12,13], the integrated intensity is then zero, this does not mean a zero XMCD spectrum (see the schematic picture in Fig. 1). Even in the presence of $5d$ electrons in
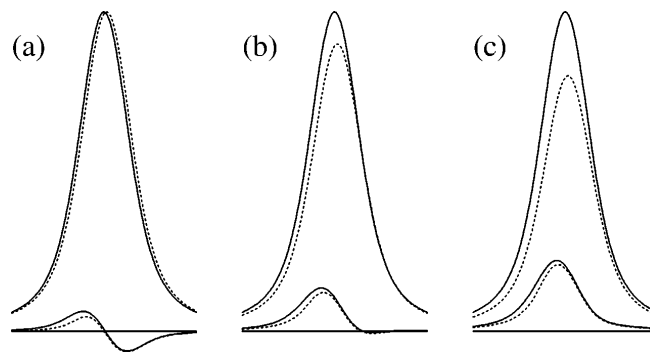

FIG. 1.   In an independent-particle picture the XMCD spectrum (solid line, bottom) is given by the difference between the spin-up (solid) and spin-down (dotted) density of states. The bands are here schematically described by a Gaussian with a FWHM of Γ, and are convoluted with a Lorentzian with a width of Γ. They are shifted with respect to each other by a df exchange of 0.075Γ. The effect of breathing (increasing β, see text) is mimicked by scaling the dipole matrix elements of the spin-down band by 1.0, 0.9, and 0.8 for (a), (b), and (c), respectively. The dotted curve at the bottom is the XMCD obtained for a filling of the bands with 0.5 electrons.

the ground state the spectrum is determined mainly by the interactions of the excited electron with the open $4f$ and $2p$ shells. This can be understood by noting that in all rare-earth compounds the $5d$ occupancy is small, and the corresponding magnetic moment of $(0.35-0.65)\mu_B$ [14] is an order of magnitude smaller than that of the $4f$ shell [$(4-10)\mu_B$]. In this Letter we present a generalization of the $5d^0$ model to metallic systems by including the contraction and expansion (the "breathing") of the $5d$ orbitals reported by Harmon and Freeman [8]. By taking into account not only the spin but also the orbital part of the Coulomb interaction we are able to explain the branching ratios of the XMCD signal.

Within a framework with fixed orbitals one can effectively create a $5d$ orbital with a different radial extent by mixing it with different d orbitals, i.e., $|5\tilde{d}\rangle = a|5d\rangle + \sum_{n\neq 5} a_n|nd\rangle$. The $5d$ orbital is coupled to the other d orbitals by the Coulomb interactions, $H_{5d,nd}$, with the open $2p$ and $4f$ shells. Band structure [8] includes only the breathing as a result of the spin part of the df interaction. This is a simplification since, as we show below, the orbital part of the df-Coulomb interaction also plays an important role.

When using the series $G = G^0(1 + H_{5d,nd}G)$ to lowest order, we find an effective dipole operator for excitations from the spin-orbit split $2p$ level (with the quantum numbers $c\gamma$, $\frac{1}{2}\sigma$ coupled to a total j and m) into the $5\tilde{d}$ orbital (with quantum numbers d and δ) by q-polarized light

$$D_{5\tilde{d},q} = \sum_{m\gamma\delta\sigma} (-)^{d-\delta+j-m}[j]^{1/2}$$
$$\times \begin{pmatrix} d & 1 & c \\ -\delta & q & \gamma \end{pmatrix} \begin{pmatrix} j & \frac{1}{2} & c \\ -m & \sigma & \gamma \end{pmatrix}$$
$$\times P_{5d}\left\{ d^{\dagger}_{5\delta\sigma} - \sum_n \frac{\beta_n}{2} H_{5d,nd}d^{\dagger}_{n\delta\sigma} \right\} c_{jm}, \quad (1)$$

with $[j] = 2j + 1$ and $\beta_n = 2P_{nd}/\Delta_{nd}P_{5d}$ with P_{nd} the reduced matrix elements of the dipole operator and Δ_{nd} the energy difference between the $5d$ and a nd orbital. $D_{5\tilde{d},q}$ reduces to the normal dipole operator $D_{5d,q}$ for $\beta_n = 0$.

The total integrated intensity for q-polarized light at a spin-orbit split edge of the XAS spectrum is

$$\tilde{I}_q^{(0)}(j) = \sum_f |\langle f|D_{5\tilde{d},q}|g\rangle|^2 = \langle g|D^{\dagger}_{5\tilde{d},q}D_{5\tilde{d},q}|g\rangle$$
$$\cong \langle g|D_{5d,q}D_{5d,q}|g\rangle$$
$$- \sum_{n\neq 5} \beta_n\langle g|D_{5d,q}H_{5d,nd}D_{nd,q}|g\rangle, \quad (2)$$

neglecting the second order terms in $H_{5d,nd}$. We see that the right hand side contains a zeroth moment (the integrated intensity of a spectrum) and a first moment. Since the final state multiplet has a small energy range, ~ 2 eV, and is heavily convoluted by the large core-hole lifetime broadening, ~ 4 eV, the XMCD line shape is

relatively simple, and the zeroth and first moments already provide a reasonable description of the spectral features.

For the integrated intensity of the circular dichroic spectrum we find

$$\tilde{I}^{(0)} = \sum_q q\tilde{I}_q^{(0)} = I^{(0)} - \sum_n \beta_n I^{(1)}(n)$$
$$= -\sum_n \beta_n I^{(1)}(n). \quad (3)$$

$I^{(0)}$ is zero since the ground state expectation values of L_z, S_z, and T_z are zero for an empty $5d$ shell [12,13]. We have thus obtained the surprisingly simple result that the shape of each edge is given by a first moment $I^{(1)}$ together with a zeroth moment $\tilde{I}^{(0)}$ which is proportional to it, and so we obtain a spectrum with a shape which is given by the β_n. When $\beta_n = 0$, the shape is purely dispersive and when the β_n increase, it evolves into a peak (see Fig. 1). For any finite value of β_n we obtain an asymmetry which is further determined by the core-hole lifetime. Within a class of related compounds the β_n should be approximately constant. Note that in the presence of breathing the filling of the $5d$ band has a relatively small effect on the integrated intensity [see Fig. 1(c)].

Let us now consider this first moment. There are various Coulomb terms that couple the $5d$ to the nd shells, but they do not have the same effect. We neglect the interaction of the $2p$ with the $5d$ since it is about five times smaller than that of the $4f$ with the $5d$ as a result of the different values for the Coulomb parameters. Of the interactions with the $4f$ shell, the direct Coulomb terms turn out to have no effect on the first moment of the circular dichroic spectrum. The first moments for the exchange part of df-Coulomb interaction can be derived using the standard techniques of Ref. [15],

$$I_{L_3}^{(1)} = 2a\langle L_z\rangle + b\langle S_z\rangle + c\langle T_z\rangle,$$
$$I_{L_2}^{(1)} = a\langle L_z\rangle - b\langle S_z\rangle - c\langle T_z\rangle, \quad (4)$$

with

$$a = \frac{1}{105}G^1 + \frac{1}{630}G^3 - \frac{5}{1386}G^5,$$
$$b = \frac{2}{105}G^1 + \frac{8}{945}G^3 + \frac{20}{2079}G^5, \quad (5)$$
$$c = \frac{2}{35}G^1 - \frac{11}{945}G^3 + \frac{25}{2079}G^5,$$

where $\langle L_z\rangle$, $\langle S_z\rangle$, and $\langle T_z\rangle$ denote expectation values of $4f$ moments and P_{5d} has been set to unity. The G^k are the df Slater exchange integrals. The sizes of the G^k depend on the element and the shell, but their ratios remain essentially constant. Therefore the ratios of a, b, and c are also constant. The result looks like an ordinary absorption sum rule as if we made transitions from $2p$ to $4f$. Furthermore, there is a proportionality to the

magnitudes of the exchange interactions. It is important to note that when $\langle L_z \rangle$ is zero the L_3/L_2 ratio is -1.

Figure 2 gives the calculated $I^{(1)}$ of the edges for all f counts using the parameter values for trivalent rare-earth ions. $\tilde{I}^{(0)}$ is proportional to $I^{(1)}$. For L_z, S_z, and T_z, we took the values calculated [16] for the atomic ground state sublevel $M = -J$, and for the G^k we took the values of Gd. We see that the value of $I^{(1)}$ varies strongly and also that the L_3/L_2 ratio take on rather extreme values (see Fig. 3). For f^7 the ratio is -1, but for light rare earths L_2 is much larger than L_3, whereas for heavy rare earths the L_3 is by far larger.

In Fig. 3 we compare our L_3/L_2 ratios with the results of a series of $R\mathrm{Fe}_2$, $R_2\mathrm{Fe}_{17}$ compounds measured by the group at the LURE synchrotron [3,4]. The experimental points have been obtained from Ref. [4]. Since the signal at some weak edges contains sign changes, we decided to define the magnitude of the circular dichroism signal as the integral of the absolute value of the XMCD spectrum. Although this causes some fortuitously good agreements, it is clear that the theory reproduces the experimental trends rather accurately.

The extreme L_3/L_2 ratios predicted by the model can be understood by an analysis in jj coupling. In the L_2 edge only $d_{3/2}$ electrons can be produced in the excitation. Because G^1 only couples electrons which differ by $\Delta j = 0, \pm 1$, there is only interaction with $f_{5/2}$ electrons/holes. For f^{13} there are no such holes and so there is no G^1 interaction and no first moment. In L_3, on the other hand, mainly $d_{5/2}$ electrons are produced which have interaction mainly with $f_{7/2}$. Here, it is f^1, where there is only an $f_{5/2}$ electron, where the first moment is small. In this case, it is not a selection rule but the circumstance that dipole and G^1 matrix elements are small between states which do not have their spin and orbit coupled in the same way, i.e., either both parallel or antiparallel: $j = l \pm s$.

We can also understand the relative magnitude of the quadrupole contributions appearing in the heavy rare earths just a few eV below the edges. Their zeroth moments are given by absorption sum rules. It is a remarkable coincidence that the value of this zeroth moment is, apart from the radial matrix element, given by Eq. (4) if we take $G^1 = -35$ and $G^3 = G^5 = 0$. Because the G^1 term gives about $\frac{2}{3}$ of the variation of the dipole intensity the quadrupole and the dipole part of the spectrum vary approximately in the same way. However, the contributions of G^3 and G^5 to the dipole part are large enough to produce interesting differences.

This can be seen in Fig. 2. In the dipolar part, L_3 and L_2 have the same signs for light rare earths and opposite signs for heavy rare earths. For f^1 to f^8 in each edge the sign of the quadrupole part is opposite to that of the dipole part. However, for f^9 to f^{13}, where the quadrupole contribution is larger, in L_2 it has the same sign as the dipole part. Furthermore, the quadrupole part is always relatively smaller in L_2. Because the quadrupole part is relatively weak, has the same sign as the dipole part, and, moreover, in L_2 the lifetime broadening is large, the two parts are not easily separated, which explains why the quadrupole part is much less readily detected in L_2 than in L_3.

The following aspects of our model deserve separate discussion.

(1) The factor β determines for a large part the shape of the edge. As was shown in recent experiments [11] the shape of the spectrum in ionic compounds is much more dispersionlike than in metals. This means that β is much smaller. Apparently β is sensitive to the surroundings. Because β is a measure for the $5d$ polarizability, and polarizability of a body is proportional to its volume, we can explain the experimental result by assuming that in an ionic compound the $5d$ orbitals are more localized and so occupy a smaller volume.

(2) Numerical calculations including configuration interaction of the $5d$ orbital with other nd orbitals support the conclusions of this paper [17]. However, for the explanation of the spectra of localized compounds we had to
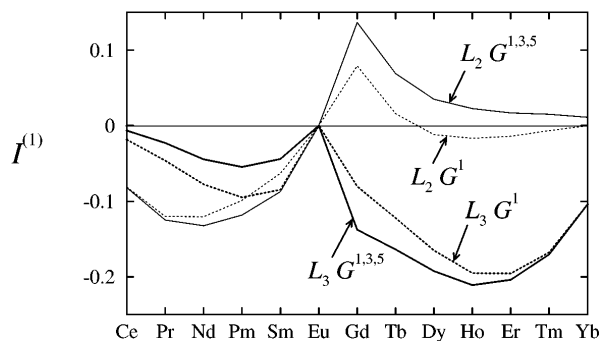

FIG. 2. The variation of the first moment $I^{(1)}$ of the $2p_j \rightarrow 5d$ circular dichroic spectrum of rare earths. The figure includes the first moment obtained using only G^1 (dotted lines) and using all G^k (solid lines) ($G^1 = 1.2, G^3 = 1.04, G^5 = 0.81$ eV).
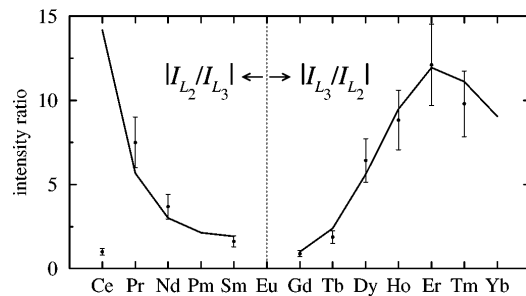

FIG. 3. Comparison of the dipolar part of the circular dichroic intensity at L_3 and L_2. The lines give the calculated ratios of the first moments; the points with error bars give the experimental ratios of the integrated absolute intensities of spectra of $R_2\mathrm{Fe}_{17}$ for Pr and Nd and $R\mathrm{Fe}_2$ for all other elements. The left panel shows $|I_{L_2}/I_{L_3}|$, the right panel $|I_{L_3}/I_{L_2}|$.

assume that the polarizability of the $5d$ orbital is strongly influenced by the solid state surroundings. Such effects seem to be best studied by band structure calculations.

(3) The large variation in L_3/L_2 ratios does not necessarily have to be calculated by atomic theory. Spin-polarized band structure theory normally includes only $5d$-$4f$ spin-spin interactions which produce an L_3/L_2 ratio of -1. This is what is observed for Gd which has a ground state which has only spin. For other f counts there are large contributions from orbit-orbit interactions which cause ratios different from -1. For a Hartree-Fock computer program employing complex basis functions, a more than half-filled $4f$ shell could simply be frozen in the single determinant Hund's rule state with $M = -J$.

(4) Apparently, in compounds with open f shells, the spectral line shape is determined predominantly by the interaction between the $5d$ and $4f$ electrons. The first effect of a finite $5d$ occupancy is to make $I^{(0)}$ in Eq. (3) nonzero. The trends of this contribution to the total integrated intensity are similar but opposite [9] to that of $I^{(1)}$. Therefore, although the XMCD signal becomes smaller, the branching ratios are not strongly affected. The effect of polarization of the $5d$ shell due to interaction with the surroundings is only clearly visible in f^0 and f^{14} compounds. Here the observation [3,4] of a large zeroth moment with a L_3/L_2 ratio of -1 almost necessarily means that there is a spin moment in the $5d$. In the case of $LuFe_2$ and $HfFe_2$, the moment needed is accurately obtained by band structure theory, which explains the $5d$ spin polarization by hybridization between the rare-earth $5d$ and the Fe $3d$ shells. This hybridization is also used to explain the antiferromagnetic alignment of rare-earth and Fe spins in RFe_2.

(5) In $CeFe_2$, a ratio of -1 is observed and a "correct" sign in accordance with the $5d$ moment predicted by band theory. Apparently, this compound falls into the f^0 class, which can be explained if we consider the ground state as a mixture of f^0 and $f^1 \underline{L}$. Then the f shell contains no moment or only a small moment, in which case the $5d$ spin polarization determines the signal. However, for γ-Ce, which is more localized, a large L_2/L_3 is found [18].

We conclude that L_3/L_2 ratios of the circular dichroism and the σ to π scattering at the rare-earth L_{23} edges are now understood much more clearly. Because of the convolution by the large $2p$ core-hole lifetime, the spectra consist of essentially one peak which can be discussed in terms of its zeroth and first moments. These have been expressed for the case of an atomic $4f^n 5d^0$ ground state. The first moment arises due to the possible parallel and antiparallel orientation of the excited $5d$ electron and the $4f$ moments. The zeroth moment arises because, for these orientations, the $5d$ electron is attracted differently by the $4f$ moments. By its polarizability, the $5d$ orbital contracts if it is attracted by the $4f$ shell, causing different radial dipole matrix elements with the $2p$ core level. Therefore, apart from their different sign,

the different orientations also get a different magnitude in the dichroism. The interactions with the $4f$ shell differ strongly in the L_3 and L_2 edges, causing a wide variety of L_3/L_2 ratios. Our mechanism of $5d$ orbital contraction is a generalization of the contraction seen in spin-polarized band structure calculations, where it is due to $5d$-$4f$ spin-spin interaction. The generalization to the complete atomic interaction, also possible in band structure calculations, is essential to explain why L_3/L_2 ratios can be strongly different from -1.

The contraction of orbitals depending on the energy of the multiplet state is an effect that should occur in any shell. But only the outermost shells are polarizable enough to give observable results, and this may be only in special, e.g., strongly delocalized environments. This could be the case for the $4p$ shell reached at the K edge of $3d$ compounds, and a model such as the one presented here may be applicable there.

With the understanding of the present model many previous experimental results have to be closely reexamined. Especially the dispersionlike character of the line shapes deserves attention as an indication of localization of the $5d$ states. Also, the quadrupole part of the L_2 edges may have to be considered. Finally, deviations from the pure d^0 L_3/L_2 ratios given here are an indication of polarization of the $5d$ electrons present in the ground state.

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